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**64 Improvements in or relating to fungicides.**

57 A method of preparing a fungicidal composition, particularly for use in treating lumber, comprises the steps of suspending a primary fungicide in a strong solvent system; adding a selected strong organic acid to the suspension to achieve a solution; and adding a surfactant system and a secondary fungicide to the solution. A fungicidal composition is also claimed, containing a primary and a secondary fungicide, both fungicides being in a true solution at high concentration, but on dilution the primary fungicide being present as an aqueous solution and the secondary fungicide as an emulsion or a suspension.

**EP 0 351 195 A2**

## Description

## Improvements in or Relating to Fungicides

This invention relates to fungicides and is intended particularly to provide a prophylactic fungicidal composition and/or a method of preparing a prophylactic fungicidal composition, for treatment of lumber and/or for relatively long term protection of lumber.

Whilst alive and still growing trees suitable for conversion to lumber are generally relatively immune from or self protected from fungal attack. After felling or after damage to the protective barrier provided by the outer layer of bark, the tree (lumber) is immediately vulnerable to attack by a variety of fungal species.

It has been practice for many years to treat felled trees, peeled logs (including poles and posts) and sawn lumber with aqueous fluids containing fungicides as a means to control said fungal attack.

Current fungicidal formulations have many disadvantages including one or more of the following:

- \* High toxicity to users;
- \* Irritant effect on users;
- \* Strong offensive odour;
- \* Corrosive to skin and some metals;
- \* Instability at higher temperatures used in some processing operations;
- \* May not control all fungi of commercial importance expected in antisapstain operations;
- \* May require separate additives to maximise fungal control.

Antisapstain chemicals are formulated to provide treating fluids which are either suspensions, emulsions or true solutions of fungicides. Each has advantages in that emulsions and true solutions offer some penetration into wood whereas suspensions provide a more concentrated barrier on the wood surface.

It is an object of the invention to provide a fungicidal composition for treatment of lumber and/or a method of preparing a fungicidal composition for treatment of lumber, which will go at least some way towards overcoming the foregoing disadvantages or which will at least provide the public with a useful choice.

Accordingly, in one aspect, the invention consists in a method of preparing a fungicidal composition, comprising the steps of:

suspending a primary fungicide in a strong solvent system; adding a strong organic acid to the suspension to achieve a solution; and adding a surfactant system and a secondary fungicide to the solution.

In a further aspect the invention consists in a fungicidal composition, comprising:

a primary fungicide and a secondary fungicide; together with a solvent/surfactant system, whereby said primary and secondary fungicides are in a true solution while said composition is relatively concentrated, but whereby when said composition is diluted said primary fungicide is principally present as an aqueous suspension, and said secondary fungicide is principally present in the form of an emulsion or

suspension.

The invention will now be more specifically described with reference to one presently preferred form of the invention.

The composition according to the invention is based preferably on substituted benzimidazole compounds as the primary fungicide, most preferably carbendazim (Methyl benzimidazol-2-ylcarbamate) but can be formulated using other substituted Benzimidazoles, such as Thlabendazole (2-(Thiazol-4-yl) benzimidazole), or chemical precursors of benzimidazoles, for example of carbendazim, including Benomyl (Methyl 1-(butylcarbamoyl) benzimidazol-2-ylcarbamate) and Thlophanate compounds for example Diethyl 4,4'-(0-phenylene) bis (3-thioallophanate).

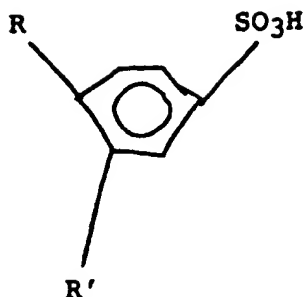
The primary fungicide can also be selected from substituted morpholinium compounds, substituted triazole compounds, substituted pyrimidine compounds, substituted imidazole compounds, substituted thiazole compounds, substituted pyridine compounds, substituted quinoxaline compounds, substituted triazine compounds, substituted guanidine compounds, substituted thiadiazole compounds and zinc or copper chelated with 8-Hydroxyquinoline which has been further reacted with certain acids, including the organic acids specified hereinafter and also including Trifluoro acetic acid and Salicylic acid.

Examples of chemicals as listed as possible primary fungicides include:

1. 4-Cyclododecyl-2,6-dimethyl morpholinium acetate
2. 4-n-Butyl-4H-1,2,4-triazole
3. 5-n-Butyl-2-dimethylamino-4-hydroxy-6-methyl pyrimidine
4.  $\alpha$ -n-Butyl- $\alpha$ -phenyl-1H-imidazole-1-propane-nitrile
5. 5-Methyl-1,2,4-triazolo [3,4b]-benzothiazole
6.  $\alpha,\alpha$ -Bis(p-chlorophenyl)-3-pyridine methanol.
7. 5,6,7,8-Tetrachloroquinoxaline
8. 4,6-Dichloro-N-(2-chloro phenyl)-1,3,5-triazin-2-amine
9. n-Dodecylguanidine
10. 5-Ethoxy-3-trichloromethyl-1,2,4-thiadiazole

During preparation the fungicide, preferably carbendazim, is reacted, in the solvent system described, with a suitable strong organic acid, preferably organic sulphonic acids or organic sulphuric acids including:

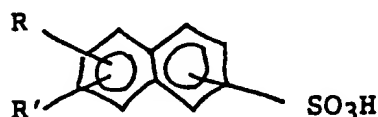
- 1) chemicals from the range of mono or di-substituted alkyl aryl sulphonic acids



where R = hydrogen, halogen, hydroxy or straight chain or branched chain aliphatic  $C_n H_{2n+1}$  where  $n = 1$  to 16

and R' = hydrogen or straight chain or branched chain aliphatic  $C_n H_{2n+1}$  where  $n = 1$  to 16

2) Naphthalene sulphonic acids of the formula:



where R and R' are defined as in 1) above

3) Aliphatic alcohol sulphuric acid half esters

4) Aliphatic and aromatic alcohol ether half esters

5) Alkane sulphonic acids

$C_n H_{2n+1} SO_3H$  where  $n = 13$  to 18

6) Olefin sulphonic acids

Preferably said acid is Dodecyl benzene sulphonic acid.

The solvent system used is preferably based on low toxicity chemicals and should preferably be of low flammability whilst retaining very strong solvent properties. The solvent or solvents or mixtures thereof chosen should have solubility parameters according to the Hansen solubility parameter system of Polar bonding greater than 2.5 and Hydrogen bonding greater than 2. Whilst a variety of solvent systems can be used those preferably used with the above properties include N-methylpyrrolidone, Cyclohexanone, Isophorone, Butyrolactone or 1,2 propylene carbonate.

Other solvents which may be used include for example 1,3 Dimethyl-2-Imidazolidone, Tetra methyl urea, Dimethyl Formamide, Dimethyl Acetamide, Dimethyl Sulphoxide, Dimethyl-2-pyrrolidone, n-Ethyl Pyrrolidone, n-Methyl-2-Piperidone and n-Methyl Caprolactam.

The presently most preferred solvent N-methyl pyrrolidone is selected to give the highest solution concentration compatible with the other expressed requirements.

A cosolvent can also be used, for example when cost is a consideration, wherein the cosolvent can reduce the overall cost when the primary solvent can be expensive. The cosolvent can be selected from the group consisting of monomeric or polymeric glycols, alcohols, glycol ethers, alcohol esters, glycol esters and aromatic solvents. Although halogenated solvents can be used these are not preferred for environmental reasons.

The surfactant system can be selected from a range of chemicals including alkyl phenol ethoxylates, aliphatic alcohol ethoxylates, copolymers of ethylene oxide and propylene oxide, alcohol esters, poly alcohol poly esters, amine ethoxylates, ester ethoxylates, and phosphate esters.

The surfactant system should have a combined hydrotrope/lipotrope balance (HLB) between 7 and 15. The preferred surfactant in this application is nonyl phenol ethoxylate (9 E.O.).

Preferably the surfactant system should be single products or simple combinations thereof where the alkyl phenol ethoxylates are chosen for low cost.

After addition of the surfactant system a secondary fungicide is added. This is preferably of low toxicity and low cost. The preferred fungicide is based on a fungicidally active metal, preferably copper or zinc, which is incorporated as a metal soap of a suitable organic acid. The organic acid can include straight chain or branched chain aliphatic carboxylic acids, substituted aromatic carboxylic acids or the preferred naphthenic acids which are also fungicidally effective.

The preferred fungicide, zinc naphthenate, may be predissolved in a small amount of turpentine or similar solvent to reduce viscosity for ease of handling.

Further examples of suitable secondary fungicides include alkyl dimethyl amines, alkyl dimethyl benzyl ammonium compounds, alkyl dimethyl benzyl ammonium compounds with substituents on the benzene ring and dialkyl dimethyl ammonium compounds, in all of the above the alkyl group being preferably aliphatic with 10 to 16 carbon atoms, and can also include substituted thiazoles for example thiocyanato methyl thio benzothiazole.

These can be substituted or partially substituted for the preferred zinc or copper naphthenates described herein.

The compounds listed as primary fungicides can be also be used as secondary fungicides by selecting an alternative primary fungicide from those specified.

The amount of organic acid required to completely solubilize a particular fungicide will vary with the fungicide selected. Optionally, an Insecticide may also be added to the composition. Suitable insecticides include, for example, synthetic pyrethroids such as permethrin, and organochlorine insecticides such as lindane.

The preferred preparation of a composition according to the invention will now be described.

The N-methylpyrrolidone is added to the mix tank and agitated slowly. The carbendazim is added slowly and mixed until complete suspension occurs. The dodecyl benzene sulphonic acid is added slowly and mixed continued until the solution becomes clear.

The reaction between the preferred carbendazim and the preferred dodecyl benzene sulphonic acid occurs at ambient temperature. The reaction is exothermic, but not generally violently so. The temperature of reaction is economically slow at very low temperatures but no practical or economic advantage is gained from adding energy to the

system other than to maintain a temperature of around 25°C. Where necessary cooling may be required to maintain moderate temperatures.

Upon completion of the reaction and cooling to ambient temperature when necessary, the surfactant system as described is added, followed by the zinc naphthenate secondary fungicide. Agitation is continued until the solution becomes uniform.

The following provides an example of the proportions of components included in a fungicidal composition according to the invention. This composition is provided by way of example only, and is not intended to be in anyway limited:

Carbendazim	7.5 parts by weight	15
Dodecyl benzene sulphonic acid	26.0 parts by weight	
N-methylpyrrolidone	37.0 parts by weight	
Nonyl phenol ethoxylate (9 E.O.)	13.0 parts by weight	20
Alkyl dimethyl amine	7.5 parts by weight	
Zinc Naphthenate (8% Zn)	9.0 parts by weight	
TOTAL	100.00 parts	25

Thus it can be seen that according to at least the preferred form of the invention a fungicidal composition for treatment of lumber and/or a method of preparing such a composition is provided, which provides a treatment using fungicides of relatively low toxicity in a solvent system giving a true solution at high concentrations, which can be readily transported and handled. A further advantage is that the treating solution formed by dilution of this concentrated composition has the benefits of both a suspension and an emulsion, in that the active ingredients are carried in two distinct phases, one aqueous and one organic. This has the advantage of providing some penetration into the wood substance as well as providing a residual barrier on the wood surface.

The fungicides used are normally soluble only with difficulty in simple solvents and can form unstable products when in combination, but the composition provided by the present invention has advantages of low toxicity, low irritancy, good thermal stability, and provides a broader spectrum of protection than known fungicidal compositions without the need for further additives at treatment stage.

The features disclosed in the foregoing description, in the following Claims and/or in the accompanying drawings may, both separately and in any combination thereof, be material for realising the invention in diverse forms thereof.

#### Claims

1. A method of preparing a fungicidal composition comprising the steps of:  
suspending a primary fungicide in a strong solvent system; adding a selected strong organic acid to the suspension to achieve a solution;

and adding a surfactant system and a secondary fungicide to the solution.

2. A method as claimed in Claim 1 wherein said primary fungicide is selected from the group consisting of substituted benzimidazoles, chemical precursors of substituted benzimidazoles, substituted morpholinium compounds, substituted triazole compounds, substituted pyrimidine compounds, substituted imidazole compounds, substituted thiazole compounds, substituted pyridine compounds, substituted quinoxaline compounds, substituted triazine compounds, substituted guanidine compounds, substituted thiadiazole compounds, and zinc or copper chelated with 8-Hydroxyquinoline; or known chemical equivalents thereof.

3. A method as claimed in Claim 1 or Claim 2 wherein said strong organic acid is selected from organic sulphonic acids organic sulphuric acids, trifluoro acetic acid and salicylic acid, said acid being selected so as to solubilize the selected fungicide to an optimally desired degree.

4. A method as claimed in any one of Claims 1 to 3 wherein said strong solvent has solubility parameters of polar bonding greater than substantially 2.5, and hydrogen bonding greater than substantially 2.0, according to the Hansen solubility parameter system.

5. A method as claimed in any one of the preceding claims wherein said surfactant system is selected from the group consisting of alkyl phenol ethoxylates, aliphatic alcohol ethoxylates, copolymers of ethylene oxide and propylene oxide, alcohol esters, polyalcohol polyesters, amine ethoxylates, ester ethoxylates, and phosphate esters.

6. A method as claimed in any one of the preceding claims wherein said surfactant system has a combined hydrotrope/lipotrope balance (HLB) of between substantially 7 and substantially 15.

7. A method as claimed in any one of the preceding claims wherein said solvent system comprises one or more primary solvents selected from the group consisting of N-methyl pyrrolidone, cyclohexanone, isophorone, butyrolactone, 1,2 propylene carbonate, dioxane, tetrahydrofuran, 1,3 dimethyl 1-2-imidazolidone, tetra methyl urea, dimethyl formamide, dimethyl acetamide, dimethyl sulphoxide, dimethyl-2-pyrrolidone, n-ethyl pyrrolidone, n-methyl-2-piperidone and n-methyl caprolactam.

8. A method as claimed in any one of the preceding claims wherein said solvent system includes a co-solvent selected from the group consisting of monomeric or polymeric glycols, alcohols, glycol ethers, alcohol esters, glycol esters and aromatic solvents.

9. A method as claimed in any one of the preceding claims wherein said secondary fungicide is selected from the group consisting of substituted benzimidazoles, chemical precursors of substituted benzimidazoles, substituted

morpholinium compounds, substituted triazole compounds, substituted pyrimidine compounds, substituted imidazole compounds, substituted thiazole compounds, substituted pyridine compounds, substituted quinoxaline compounds, substituted triazine compounds, substituted guanidine compounds, substituted thiadiazole compounds, zinc or copper chelated with 8-Hydroxyquinoline, alkyl dimethyl amines, alkyl dimethyl benzyl ammonium compounds, alkyl dimethyl benzyl ammonium compounds having substituents on the benzene ring, dialkyl dimethyl ammonium compounds, and substituted thiazoles; or known chemical equivalents thereof.

10. A method as claimed in any one of the preceding claims including the further step of adding an insecticide to the solution.

11. A method as claimed in any one of the preceding claims wherein said fungicides are of relatively low toxicity.

12. A method of preparing a fungicidal composition, substantially as hereinbefore described with reference to the example.

13. A fungicidal composition, comprising: a primary fungicide and a secondary fungicide; together with a solvent/surfactant system, whereby said primary and secondary fungicides are in a true solution while said composition is relatively concentrated, but whereby when said composition is diluted said primary fungicide is principally present as an aqueous suspension and said secondary fungicide is principally present in the form of an emulsion or as a suspension.

14. A composition as claimed in Claim 13 wherein said primary fungicide is selected from the group consisting of substituted benzimidazoles, chemical precursors of substituted benzimidazoles, substituted morpholinium compounds, substituted triazole compounds, substituted pyrimidine compounds, substituted imidazole compounds, substituted thiazole compounds, substituted pyridine compounds, substituted quinoxaline compounds, substituted triazine compounds, substituted guanidine compounds, substituted thiadiazole compounds, and zinc or copper chelated with 8-Hydroxyquinoline which has been further treated with an organic sulphonic acid, an organic sulphuric acid, trifluoro acetic acid or salicylic acid; or known chemical equivalents thereof.

15. A composition as claimed in Claim 13 or 14 wherein said strong organic acid is an organic sulphonic acid or an organic sulphuric acid.

16. A composition as claimed in any one of Claims 13 to 15 wherein said strong solvent has solubility parameters of polar bonding greater than substantially 2.5, and hydrogen bonding greater than substantially 2.0, according to the Hansen solubility parameter system.

17. A composition as claimed in any one of Claims 13 to 16 wherein said surfactant system is selected from the group consisting of alkyl

phenol ethoxylates, aliphatic alcohol ethoxylates, copolymers of ethylene oxide and propylene oxide, alcohol esters, polyalcohol polyesters, amine ethoxylates, ester ethoxylates, and phosphate esters.

18. A composition as claimed in any one of Claims 13 to 17 wherein said surfactant system has a combined hydrotrope/lipotrope balance (HLB) of between substantially 7 and substantially 15.

19. A composition as claimed in any one of Claims 13 to 18 wherein said solvent system comprises one or more primary solvents selected from the group consisting of N-methyl pyrrolidone, cyclohexanone, isophorone, butyrolactone, 1, 2 propylene carbonate, dioxane, tetrahydrofuran, 1,3 dimethyl 1-2-imidazolidone, tetra methyl urea, dimethyl formamide, dimethyl acetamide, dimethyl sulphoxide, dimethyl-2-pyrrolidone, n-ethyl pyrrolidone, n-methyl-2-piperidone and n-methyl caprolactam.

20. A composition as claimed in any one of Claims 13 to 19 wherein said solvent system includes a co-solvent selected from the group consisting of monomeric or polymeric glycols, alcohols, glycol ethers, alcohol esters, glycol esters and aromatic solvents.

21. A composition as claimed in any one of claims 13 to 20 wherein said secondary fungicide is selected from the group consisting of substituted benzimidazoles, chemical precursors of substituted benzimidazoles, substituted morpholinium compounds, substituted triazole compounds, substituted pyrimidine compounds, substituted imidazole compounds, substituted thiazole compounds, substituted pyridine compounds, substituted quinoxaline compounds, substituted triazine compounds, substituted guanidine compounds, substituted thiadiazole compounds, zinc or copper chelated with 8-Hydroxyquinoline, alkyl dimethyl amines, alkyl dimethyl benzyl ammonium compounds, alkyl dimethyl benzyl ammonium compounds having substituents on the benzene ring, dialkyl dimethyl ammonium compounds, and substituted thiazoles; or known chemical equivalents thereof.

22. A composition as claimed in any one of Claims 13 to 21 also including an insecticide.

23. A composition as claimed in any one of Claims 13 to 22 wherein said fungicides are of relatively low toxicity.

24. A fungicidal composition substantially as hereinbefore described with reference to the example.

25. A method of treatment of lumber and/or protecting lumber relatively long term, which method comprises treating lumber with a fungicidal composition in accordance with any one of Claims 13 to 23 and/or prepared by a method in accordance with any one of Claims 1 to 11.